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OPACIFIED GLAZES PRODUCED BY HIGH-TEMPERATURE FIRING FOR SANITARY CERAMICWARE

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The possibility of producing glaze coatings for sanitary ceramicware without using toxic compounds, such as barium carbonate and zinc white, is discussed. The regularities of variations in the physicochemical properties of glazes (luster, whiteness, microhardness, TCLE) depending on their chemical composition are identified in correlation with their structural specifics and phase composition.

At present opacified glaze coatings concealing the base color and providing good decorative properties of glazed products are used to decorate most household ceramic products. Sanitaryware is usually produced using non-fritted opacified glazes, which is related to a high temperature and a longer heat treatment than those used in firing other traditional ceramics. It should be noted that despite the diversity of known glazes [1–3], virtually all of them contain hazardous components: barium carbonate BaCO_3 (I class of hazard) and zinc white ZnO (II class of hazard). Therefore, the synthesis of opacified coatings not containing the above components and having a high degree of whiteness is a topical problem.

Zirconium compounds are extensively used as opacifying agents in glaze production. Zirconates have a favorable effect on chemical and thermal resistance, mechanical strength, luster, and other properties of coatings. A high degree of opacity can be obtained by mixing zircon with alkali and alkaline-earth metal oxides previously calcined at a temperature of 1200–1250°C. Foreign companies offer such opacifiers under various trademarks, such as Meltopax, Zircosil SA, or Zircosil S [4]. In these compounds, a preliminary reaction between zirconium carbonate and silicate has occurred, which facilitates the process of firing and provides certain advantages in using non-fritted glazes.

It is known [3] that the intensity of glaze opacification primarily depends on the difference between the refractive indexes of the opacifying particles and the main glass. However, despite the high refractive index of zirconium dioxide ($n = 2.4$), one cannot always obtain the required degree of opacification, which is due to the limited solubility of ZrO_2 in silicate melts. Some literature sources [3–5] report that the ultimate solubility of zirconium dioxide is 3–5% (here

and elsewhere weight content is indicated) and depends on the type and quantity of other components. Thus, Al_2O_3 , ZnO , MgO , and alkali metal oxides decrease the solubility of ZrO_2 in glass [5]. Hence it follows that depending on the chemical composition of glaze coatings, various conditions may arise, where crystallization of ZrO_2 and its compounds is observed. This is even more true for non-fritted glazes, whose firing temperature is 1200°C, so it can be assumed that the full dissolution of zirconium dioxide and other components (quartz, pegmatite, kaolin) in the melt does not occur.

The degree of opacification of a zirconium glaze to a large extent depends on the dispersion and uniformity of the distribution of the fine-crystalline opacifier phase. For complete opacification, opacifier grains should be as small as possible. It should be noted that the degree of opacification of glazes depends not so much on the high content of the crystalline phase, but on its total surface area. The smaller the particle size, the more perceptible is light scattering occurring due to the reflection of light from the finest particles of the heterogeneous mixture in a colloid, fine-crystalline, or gaseous state and, accordingly, the higher is the degree of opacification of the glaze [6].

The purpose of our study was to develop opacified zirconium glazes for sanitary ceramics not containing toxic components (barium carbonate, zinc white) and fired at a temperature of 1200°C, to identify the mechanism of glaze opacification, and to determine the effect of chemical composition on glaze properties. The opacifier introduced in glazes was zircosil (Italy) of the following chemical composition (%): 36.88 SiO_2 , 0.60 Al_2O_3 , 0.14 TiO_2 , 0.11 Fe_2O_3 , and 62.27 ZrO_2 .

The identification of glaze-formation ranges was performed in three sections of a system of components including pegmatite, quartz sand, and chalk with zircosil content equal to 10.0, 12.5, and 15.0% and a constant content of talc,

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refractory clay, and kaolin equal to 5.5, 5.5, and 4.5%, respectively. The quantity of the main components varied in the following limits (%): 25.0 – 37.5 pegmatite, 17.5 – 30.0 quartz sand, and 7.5 – 22.5 chalk.

Glazes were prepared by joint moist milling of components in a ball mill to a residue of 0.1% on a No. 0056K sieve. To ensure the required flow properties of the glaze suspension, 0.15% sodium tripolyphosphate was introduced in the suspension. To obtain a pure white color under artificial lighting, 0.015% cobalt sulfate was additionally introduced into the mixture. Sodium tripolyphosphate and cobalt sulfate were added above 100% of glaze components.

After magnetic concentration, the suspension was cast on a porcelain base dried to a residual moisture not more than 1%. The glazed samples were fired in a module-type tunnel furnace produced by Sacmi (Italy) under industrial conditions at the Keramin JSC. The lining of this furnace consists of effective fibrous refractories; the furnace cars have an extended bottom designed as a one-tier stack made of refractory plates. The overall furnace dimensions are: length 98.8 m, channel width 2.9 m, height 0.8 m, the number of cars in the furnace — 76. With the pushing frequency of 88 cars per day, the firing regime was as follows: heating duration 10 h, exposure at the maximum temperature of 1180 – 1200°C 5 h, and cooling 7 h.

To study the processes occurring under heating glaze mixtures, differential thermal analysis was performed. The thermograms in the temperature interval of 220 – 450°C exhibit an endothermic effect related to the removal of constitution water and the destruction of argillaceous minerals. The second endothermic effect at a temperature of 495 – 520°C is determined by the polymorphic transformation of quartz. The final endothermic effect at the temperature of 760 – 770°C is related to the decomposition of calcium carbonate $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$. The beginning of the formation of the new crystalline phase, i.e., zircon ZrSiO_4 , is characterized by the exothermic effect at a temperature of 835 – 890°C. As the content of zircosil in the glaze grows, this exothermic effect is shifted to a higher-temperature range: 940 – 960°C.

The result of firing glaze costing demonstrated that they have different degrees of opacification for all sections, sufficiently uniform spreading, and relatively high whiteness.

The luster and whiteness of coating were determined using a BF-2 photoelectric luster meter. Microhardness was investigated using a PTM-3M microhardness gage with a FOM-2 photoelectron micrometer. The CLTE was measured on a DIL 402PC electron dilatometer (NETZSCH), the readings of the instrument were recorded automatically and shown on a computer display.

The dependences of luster, whiteness, and microhardness of glaze coating on their compositions are represented as equal-value lines (Fig. 1). Whiteness varied within the limits of 60 – 77% for coating luster of 45 – 70%. It can be seen in Fig. 1 that the luster and whiteness parameters regularly

grow with growing content of quartz and pegmatite at the expense of chalk, which has a perceptible effect on the specified properties: an increasing quantity of CaO decreases the luster.

In all sections of the system one can see the formation of both lustrous (luster above 60%) and semidull surfaces. The decrease in luster and the formation of semidull coatings are presumably due to a large number of pinholes on the glaze glass surface, which can be explained by the migration of small gaseous bubbles, which arise in disassociation of carbonates, from the depth of the glaze layer toward its surface. Small craters in this case do not have time to fuse; accordingly, more or less perceptible pinholes remain after cooling. Since all samples were fired in equal conditions, evidently the tendency to pinholes is caused by the materials used. It has been established that introducing above 17.5% chalk is unadvisable, since it leads to a perceptible decrease in luster. Another reason for coating dullness can be the formation of large opacifier crystals.

The highest whiteness parameters (70 – 75%) are registered in the compositions constructed in the first section, which have the $\text{SiO}_2 : \text{Al}_2\text{O}_3$ ratio equal to 7.2 – 7.6 and a minimal content of ZrO_2 (6.2%).

The microhardness of all experimental series of glazes is approximately equal and amounts to 6500 – 7500 MPa. Its increase is observed on increasing the content of SiO_2 at the expense of CaO.

The analysis of the chemical compositions of all considered sections of glazes identified the optimal ratios of oxides $(\text{SiO}_2 + \text{ZrO}_2) : (\text{R}_2\text{O} + \text{RO})$ amounting to 4.3 – 5.6, where R_2O is the sum of Na_2O and K_2O , and RO is the sum of CaO and MgO. With such ratios, satisfactory properties of coatings are registered.

For an approximate estimate of the CLTE, its values were theoretically calculated according to A. A. Appen's method using partial coefficients [7]. The CLTE of the glazes in the first section, which have enhanced whiteness, is $(45 - 62) \times 10^{-7} \text{ K}^{-1}$, that of the coatings of the second section is $(43 - 60) \times 10^{-7} \text{ K}^{-1}$, and in the third section $(40 - 59) \times 10^{-7} \text{ K}^{-1}$. Note the discrepancy between the estimated and experimental data: the difference amounts to $(2 - 5) \times 10^{-7} \text{ K}^{-1}$. This is presumably due to the fact that such calculations are applicable to glasses with completely homogenized melts, whereas non-fritted glazes probably do not meet this requirement. Despite the discrepancy between the estimated and experimental data, a general regularity is observed in CLTE variations depending on glaze compositions. The comparative analysis of the CLTE of the ceramic base equal to $(56 - 62) \times 10^{-7} \text{ K}^{-1}$ and the CLTE of synthesized coatings shows that most of them satisfy the requirements on the compatibility of thermal expansion of coating and the ceramic base. It is known that the CLTE of glazes should be 10% lower than the CLTE of the ceramic base, which ensures high thermal strength of glaze coatings.

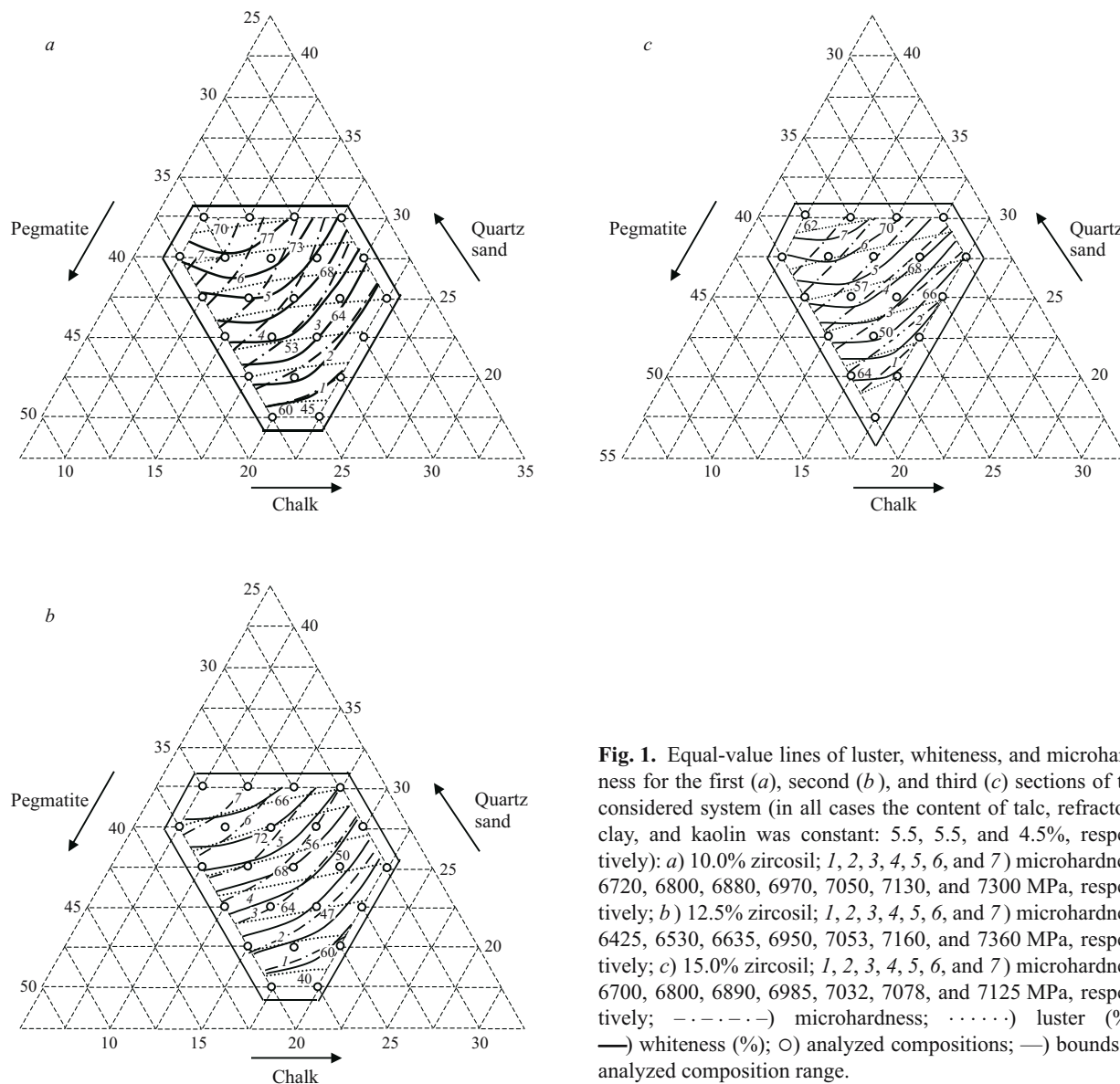


Fig. 1. Equal-value lines of luster, whiteness, and microhardness for the first (a), second (b), and third (c) sections of the considered system (in all cases the content of talc, refractory clay, and kaolin was constant: 5.5, 5.5, and 4.5%, respectively): a) 10.0% zirconium; 1, 2, 3, 4, 5, 6, and 7) microhardness 6720, 6800, 6880, 6970, 7050, 7130, and 7300 MPa, respectively; b) 12.5% zirconium; 1, 2, 3, 4, 5, 6, and 7) microhardness 6425, 6530, 6635, 6950, 7053, 7160, and 7360 MPa, respectively; c) 15.0% zirconium; 1, 2, 3, 4, 5, 6, and 7) microhardness 6700, 6800, 6890, 6985, 7032, 7078, and 7125 MPa, respectively; — · — · — · —) microhardness; · · · · ·) luster (%); —) whiteness (%); ○) analyzed compositions; —) bounds of analyzed composition range.

The x-ray phase analysis established that the main crystalline phase in the considered glazes is zircon; furthermore, a small quantity of α -quartz is present as well. It is notable that as the zirconium content in glazes grows from 10% in the first section to 15% in the third section, the relative intensity of the diffraction maximums of zircon decreases, which points to a decreasing quantity of the newly formed crystalline phase. Hence, the optimum content of ZrO_2 in the considered glazes is 6.2%. This is corroborated by published data [5]: zircon in the absence of crystallization modifiers becomes well crystallized from the melt upon introducing 2 – 7% ZrO_2 .

The electron-microscope study of the structure of samples was carried out by electron probe microanalysis on a JSM-5610 LV scanning electron microscope equipped with a EDX JED-2201 JEOL chemical analysis system (Japan).

The study of glaze structure by electron microscopy corroborated the data of x-ray phase analysis and established that the opacification of coatings occurs only through crystallization.

The study of the structure of coatings with different contents of zirconium indicates that the most complete and homogeneous crystallization of zircon takes place in the glaze with 10% zirconium, which is introduced via 6.2% ZrO_2 . Raising the zirconium content from 10% (6.2% ZrO_2) to 15% (9.3% ZrO_2) decreases the content of crystalline formations in the glaze layer from 40% to approximately 7%, respectively, which is visible in the electron microscope photos (Fig. 2).

Glazes in the first section exhibit the presence of large α -quartz crystals of a shape close to prismatic. The size of these crystals is up to $5 \times 2 \mu\text{m}$; however, their content is not more than 5 – 7% of the total amount of the crystalline components. The crystalline phase is mainly represented by fine

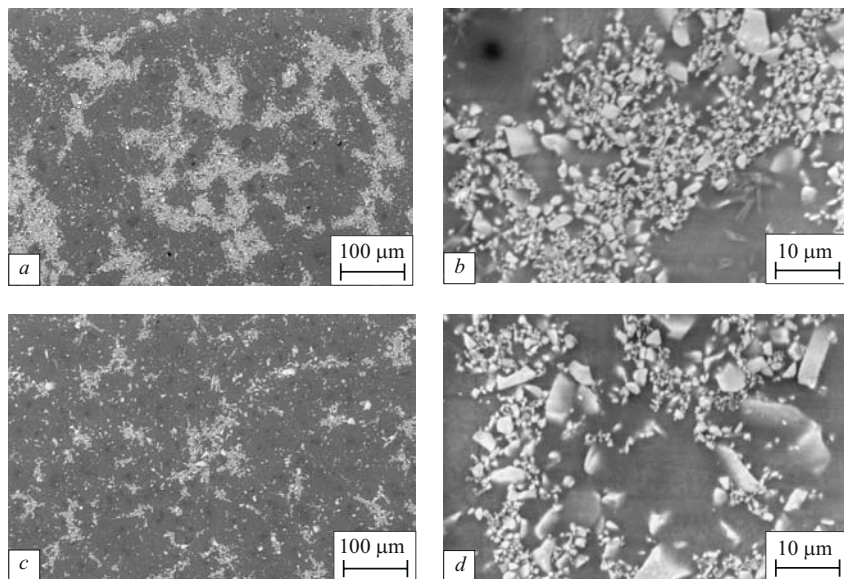


Fig. 2. Electron microscope photos ($\times 200$) of surfaces of glaze coatings with zircosil content of 10% (*a, b*) and 15% (*c, d*).

isometric crystals of zircon whose size varies from 0.1 to 0.4 μm ; they are responsible for the degree of opacity of the surface. In glazes of the third section, crystals despite the similar shape are larger and their content is significantly lower. Thus, the size of large crystals is $10 \times 3 \mu\text{m}$, that of small crystals 0.2 – 0.5 μm , and the relative content of large crystals grows to 10 – 12% of the total quantity of the crystalline phase. Semidull coatings are formed in this section, which is presumably due to significant reflection of light by the facets of large crystals and the presence of pinholes.

The decreasing degree of opacification in coatings with an increasing content of zircosil in glazes is presumably due to the growing viscosity of the melt, which decreases its crystallization capacity. It should be noted that the rate of crystal growth is determined by the diffusion of zirconium ions from the melt. The diffusion coefficient of ZrO_2 is one of the highest, which is due to a large quantity of oxygen ion vacancies. As the viscosity and density of the melt grow, the diffusion rate substantially decelerates, which decreases the degree of crystallization [5]. This conclusion is corroborated by studying the distribution and concentration of chemical elements in the structure of glaze coatings. The element composition of samples was analyzed based on their characteristic radiation spectra. The qualitative composition of samples was determined based on the K-line position in the analyzed spectrum and the quantitative composition was estimated based on the intensity of these lines.

The obtained results show that in coatings with a higher degree of opacification, nearly all zirconium introduced via

zircosil is concentrated in the crystalline phase, whereas its content in the vitreous phase is not higher than 2%. As the opacification of glaze decreases, the amount of zirconium in the vitreous phase grows and reaches 16%.

The following mechanism of glaze opacification is assumed. Zirconium dioxide in melting presumably becomes dissolved in the silicate melt and in cooling is again formed as zircon crystals ZrSiO_4 .

It is established that glazes in the first section containing over 20% chalk do not satisfy the required heat stability: crackle is observed in samples after two-time boiling in 50% calcium chloride solution, which is related to the CLTE of the coating growing due to the increasing CaO content. As the quantity of zircosil grows to 12.5 and 15.0% (the second and third sections), all compositions become thermally stable, which is due to the decreased CLTE of the coating and its compatibility with

the CLTE of the ceramic base. This is achieved by raising the content of ZrO_2 in the vitreous phase.

The study of the chemical resistance of glaze coatings determined by a parallel exposure of samples for 1 h in three solutions: in 20% H_2SO_4 , 20% HCl, and 5% KOH demonstrated that glazes of all series satisfy the requirements of GOST 15167–93 standard.

Thus, opacified glazes not containing toxic agents (barium carbonate, zinc white) can be used to decorate sanitary ceramics. The integrated study of the physicochemical properties of coatings identified the optimum ranges in the first section of glaze compositions with 10% zircosil content providing glazes whose quality meets the requirements of production specifications.

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